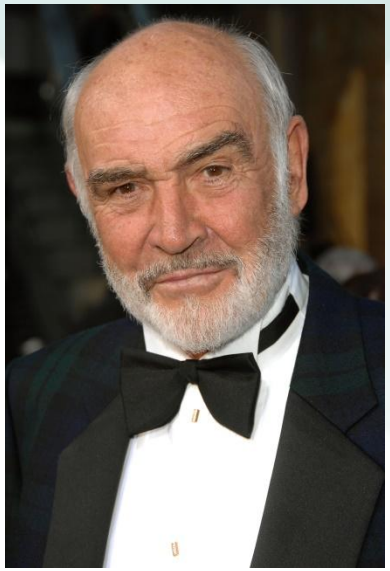

FERNÁNDEZ CASCÁN, JESÚS

Technical staff (Geologist)

LIFE SURFING PROJECT: SURFACTANT ENHANCED CHEMICAL OXIDATION FORREMEDIATING DNAPL. PREPARATORY WORK

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14th International HCH and Pesticides Forum

WHAT IS LIFE SURFING?

"SURFactant enhanced chemical oxidation for remediatING DNAPL"

Demonstration project for the application of S-ISCO techniques (combination of surfactants and oxidants) in fractured media with the presence of DNAPL

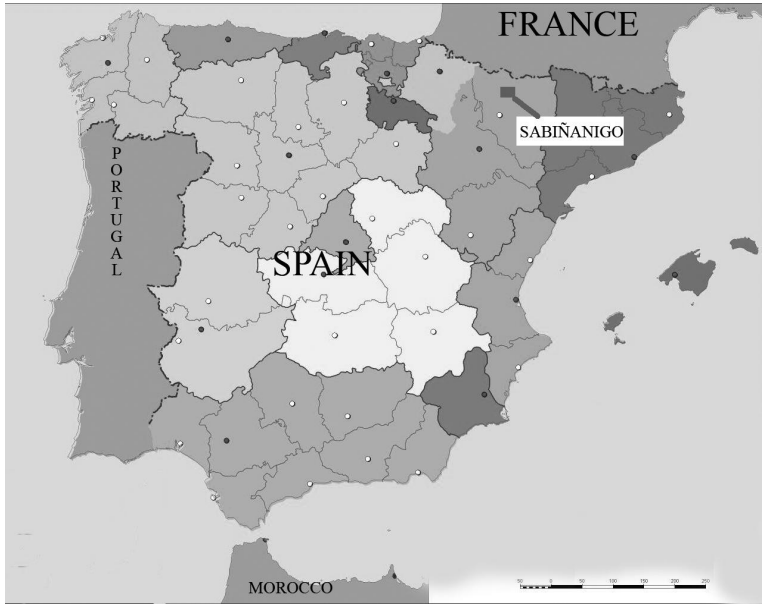
Proyecto demostrativo para la aplicación de técnicas S-ISCO (combinación de surfactantes y oxidantes) en medios fracturados con presencia de DNAPL

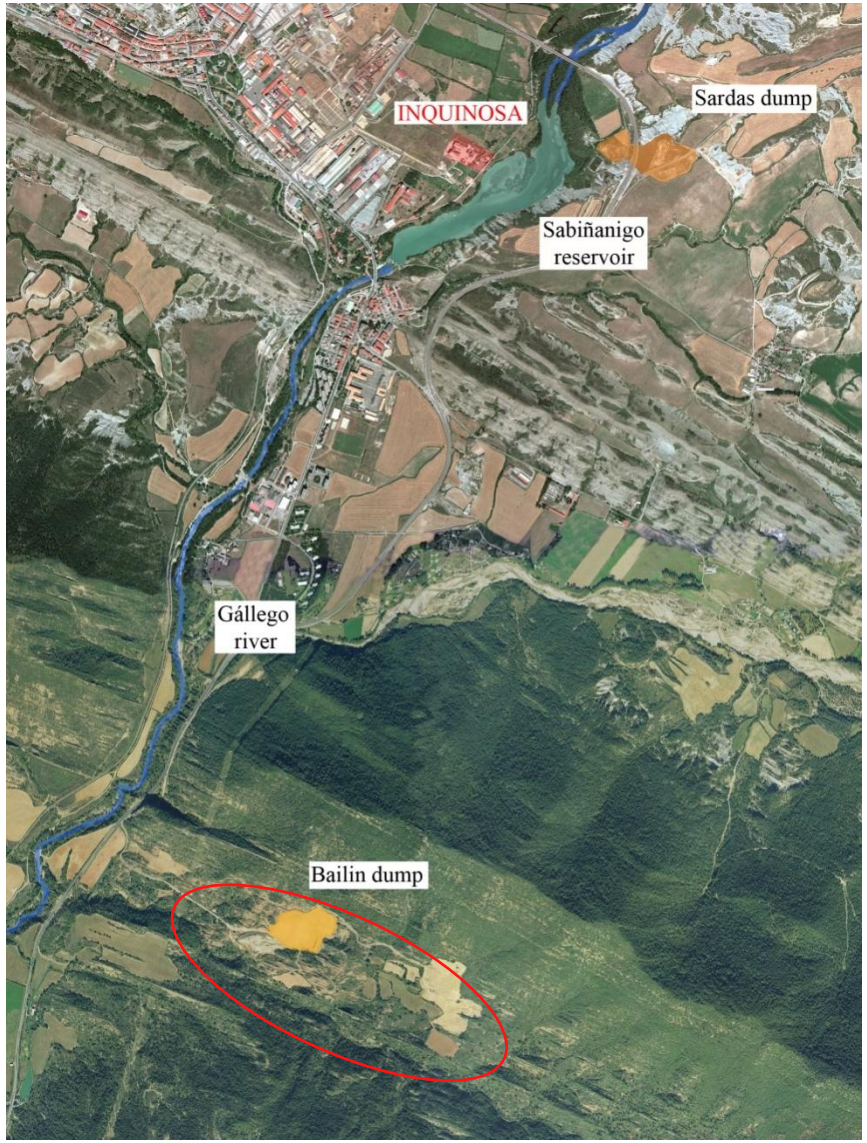
FLIX.NET

PRESENT: a LIFE production

Chap 1: Phase 0 - PREPARATORY WORK
Chap 2: Phase 1: Surfactant Enhanced Extraction (SEAR)
Chap 3: Phase 2: Surfactants + oxidants (S-ISCO)

GEOGRAPHIC LOCATION

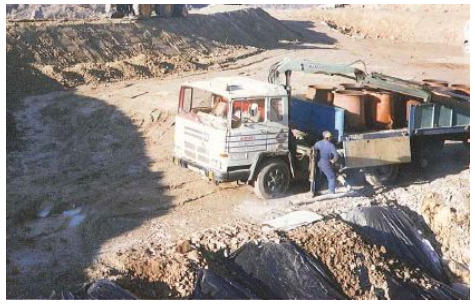




Main sources of lindane manufacturing waste:

- **OLD INQUINOSA FACTORY**
- **SARDAS LANDFILL**
- **BAILIN LANDFILL**

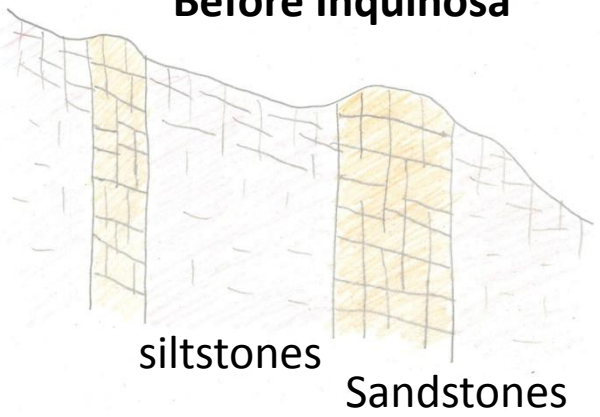
BASIC DATA



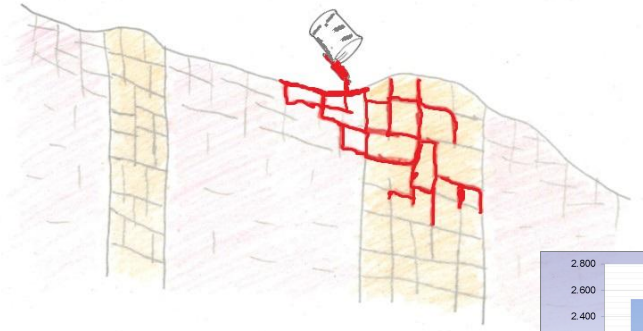
* PERIOD OF OPERATION: 1984-1992
* TOTAL WASTE 200,000 m^3
  * URBAN 20,000 m^3
  * SOLID WASTE OF HCH 64,000 t
  * LIQUID WASTE WITH HCH (DNAPL) 2,000-3,000 t
  * CONTAMINATED LANDS 342,000 t
* WITHOUT INSULATION AT THE BASE
* SURFACE COVER WITH HDPE SHEET IN 1996
* DNAPL PRESENCE
* NEAR THE RECEIVER CHANNEL: Gállego river at 800 m

WHAT HAPPENED? WHERE WE ARE?

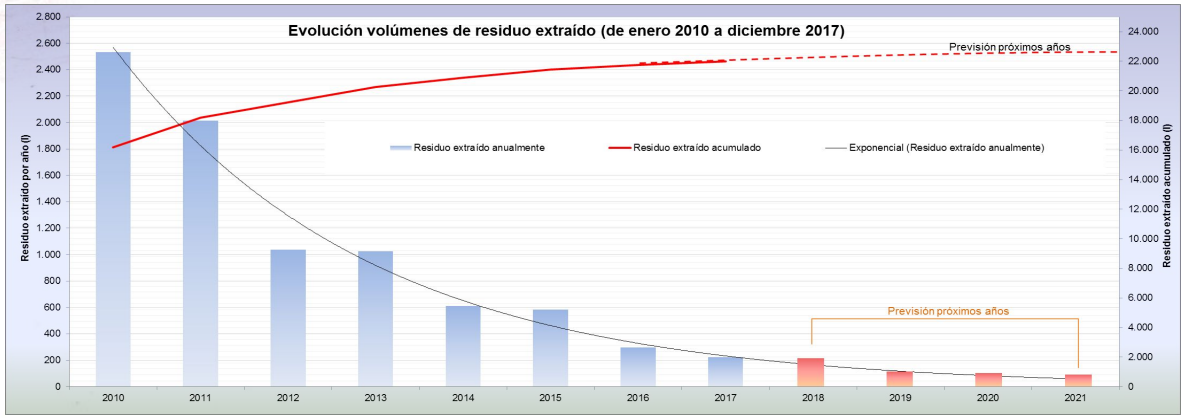
Before Inquinosa



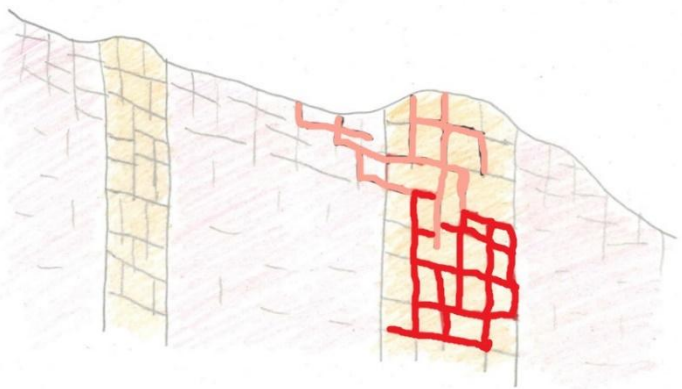
with INQUINOSA



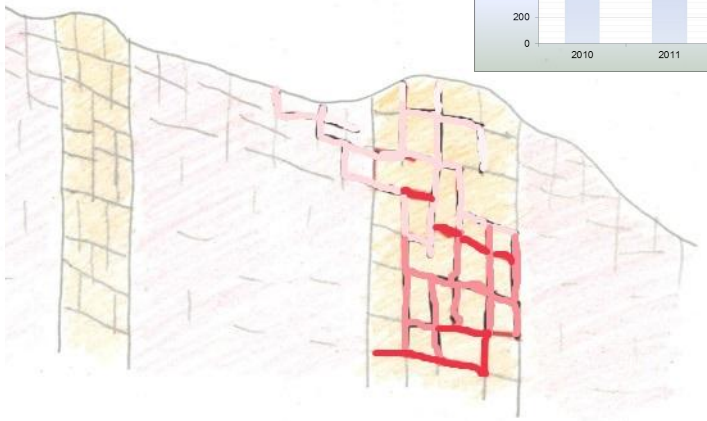
Evolution of DNAPL extraction



Before detecting DNAPL



In 2021



Phase 0 - PREPARATORY WORK

- **Experimental design:**
  - ✔ Review of hydrogeological and geochemical data from the test area.
  - ✔ SEAR, S-ISCO literature review and research carried out by the team.
  - ✔ Analysis of possible on-site treatment techniques
  - ✔ Tests of applicable barrier techniques
  - ✔ Definition of the test area
- **Execution of boreholes and infrastructures**
- **Base line of the test zone and layer M**
  - ✔ Hydrogeological tests
  - ✔ Tracer test

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EXPERIMENTAL DESIGN: DNAPL characterization

Peaks and acronym of compounds identified in the chromatogram of the DNAPL sample

	tR FID	tr GC/MSD	Acronim	Name	CAS	MW
1	1.48	2.51	CB	chlorobenzene	108-90-7	112.0
2	2.27	3.56	1,3 DCB	1,3-dichlorobenzene	541-73-1	146.0
3	2.31	3.63	1,4 DCB	1,4-dichlorobenzene	106-46-7	146.0
4	2.41	3.73	ISTD	butylcyclohexane	1678-93-9	140.3
5	2.47	3.82	1,2 DCB	1,2-dichlorobenzene	95-50-1	146.0
6	3.21	4.69	1,3,5 TCB	1,3,5-trichlorobenzene	108-70-3	179.9
7	3.59	5.11	1,2,4 TCB	1,2,4-trichlorobenzene	120-82-1	179.9
8	3.91	5.47	1,2,3 TCB	1,2,3-trichlorobenzene	87-61-6	179.9
9	4.95	6.56	TetraCB-a	1,2,4,5 tetrachlorobenzene /1,2,3,4 tetrachlorobenzene	95-94-3/ 634-66-2	214.0
10	5.40	7.05	TetraCB-b	1,2,3,5 tetrachlorobenzene	634-90-2	214.0
11	6.11	7.87	g-PentaCX	g-pentachlorocyclohexene	342631-17-8	252.0
12	6.68	8.70	PentaCB	1,2,3,4,5 pentachlorobenzene	608-93-5	247.9
13	6.76	8.81	δ-PentaCX	δ-Pentachlorocyclohexene	643-15-2	252.0
14	7.05	9.29	θ-PentaCX	θ-Pentachlorocyclohexene	319-94-8	252.0
15	7.21	9.46	HexaCX-a	Hexachlorocyclohexene	1890-41-1	288.8
16	7.32	9.62	β-PentaCX	β-Pentachlorocyclohexene	319-94-8	252.0
17	7.51	9.96	η-PentaCX	η-Pentachlorocyclohexene	54083-24-8	252.0
18	8.12	10.93	HexaCX-b	Hexachlorocyclohexene	1890-41-1	286.0
19	8.40	11.43	HexaCX-c	Hexachlorocyclohexene	1890-41-1	286.0
20	8.50	11.64	a-HCH	a-hexachlorocyclohexane	319-84-6	291.0
21	8.84	12.20	HexaCX-d	Hexachlorocyclohexene	1890-41-1	286.0
22	9.25	12.87	β-HCH	β-hexachlorocyclohexane	319-85-7	291.0
23	9.43	13.17	g-HCH	g-hexachlorocyclohexane (Lindane)	58-89-9	291.0
24	9.71	13.68	HeptaCH-1	Heptachlorocyclohexane	707-55-1	322.0
25	10.20	14.47	δ-HCH	δ-hexachlorocyclohexane	319-86-8	291.0
26	10.54	15.12	e-HCH	e-hexachlorocyclohexane	6108-10-7	291.0
27	11.18	16.30	HeptaCH-2	Heptachlorocyclohexane	707-55-1	322.0
28	12.11	17.96	HeptaCH-3	Heptachlorocyclohexane	707-55-2	322.0

Composition of DNAPL samples from the Bailín landfill

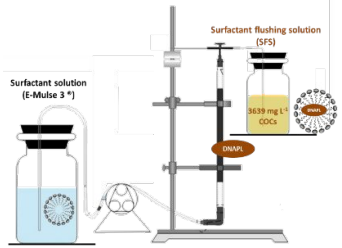
		BAILIN-O1 (UCM)-2018	BAILIN-20 /03/19	BAILIN-11/ 09/19
Bencene	%	na	na	na
CB	%	10.40	11.19	11.26
1,3 DCB	%	0.20	0.39	0.31
1,4 DCB	%	2.10	2.60	2.46
1,2 DCB	%	1.70	1.78	1.57
1,3,5 TCB	%	0.00	0.06	0.07
1,2,4 TCB	%	5.50	6.07	5.73
1,2,3 TCB	%	0.50	0.77	0.56
TetraCB (1,2,3,5 + 1,2,4,5)	%	1.40	2.19	2.01
TetraCB (1,2,3,4)	%	2.40	2.70	2.54
PentaCB	%	0.20	0.46	0.32
∑-PentaCX	%	13.30	14.82	15.05
∑-HexaCX	%	5.20	3.71	3.17
∑-HeptaCH	%	26.70	25.50	28.22
α-HCH	%	4.40	4.47	4.43
β-HCH	%	0.03	0.00	0.00
γ-HCH	%	14.00	14.26	13.19
δ-HCH	%	10.70	7.72	7.87
ε-HCH	%	1.50	1.30	1.24

EXPERIMENTAL DESIGN: Selection of surfactant

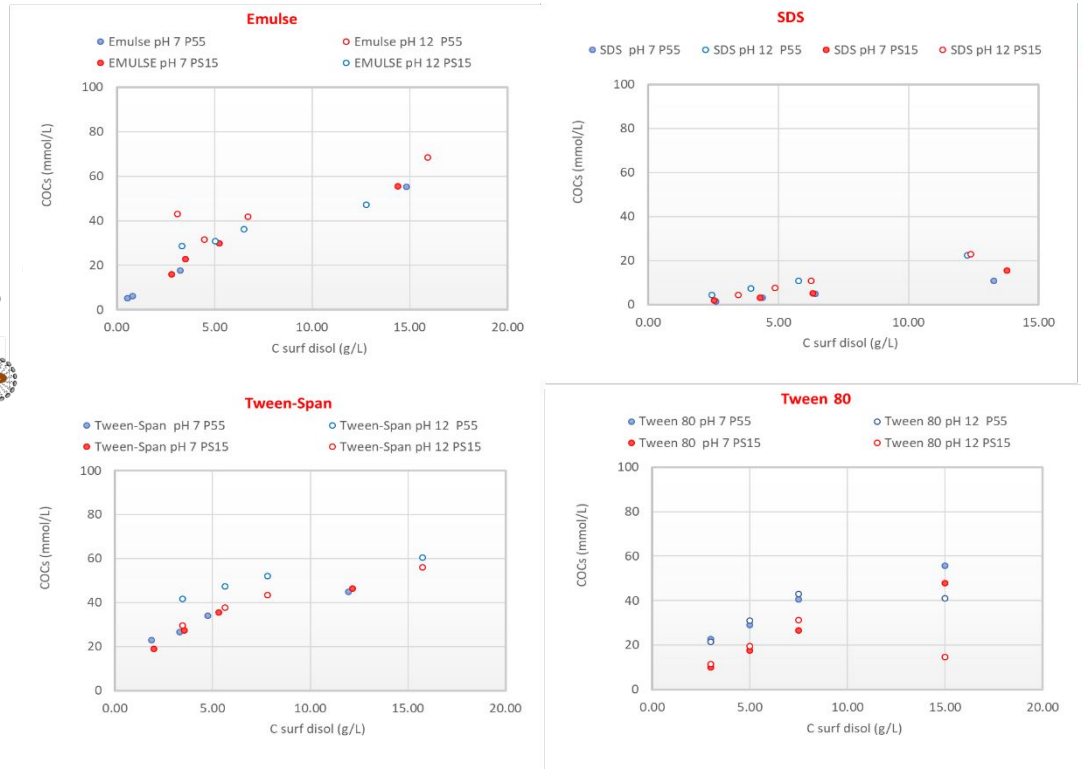
Since 2018: previously selected surfactants (Tween-Span, SDS) plus E-Mulse 3 ® proposed by UCM. Bacht and column tests: solubilization of DNAPL, CMC, behavior against pH, unproductive consumption with oxidants, stability of emulsions,..

COCs concentration (g/l) with and without surfactant for two DNAPL samples

P55 (Bailin)			
Initial C Surfactant (g/L)	0 g/L	3 g/L	15 g/L
Emulse-3 ®	119	1182	13446
SDS	119	244	2560
Tween 80	119	5338	12829
Tween (35%)-Span (65%)	119	5549	7700
PS15 (Sardas)			
Initial C Surfactant (g/L)	0 g/L	3 g/L	15 g/L
Emulse-3 ®	130.2	3100	10906
SDS	130.2	300	2819
Tween 80	130.2	1830	8891
Tween (35%)-Span (65%)	130.2	3712	9188



Stability at alkaline pH



Taking into account the set of properties, the SDS is discarded, E-MULSE ® is selected for its good biodegradability and ease of handling compared to Tween 80, Span 80 or mixtures of both.

DEFINITION OF THE TEST AREA

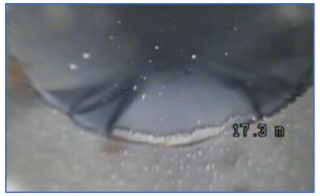
CRITERIA	M layer	I layer
presence of residual DNAPL		
Existing boreholes		
Lithological information, fracturing, etc.		
Longitudinal development of the layer		
Ease of drilling new boreholes		
Ease of access		
Connectivity between boreholes		
Proximity to facilities		

Initial hypothesis: the axis of the W gully is the most favorable zone for locate DNAPL due to fracturing and topography.

DRILLING AND TESTING BOREHOLES

Conditions:

- Drilling to 130 mm diameter with core recovery.
- All boreholes in sandstone layer:
  - It is not necessary to equip them
  - Packers can be used.
  - Connectivity between boreholes will be good.
- Lugeon tests: permeability
- Merc tests: methanol extraction rock cores, absorbed COPs?
- Odor, presence of DNAPL
- Fracture and lithology testing: on cores, with video

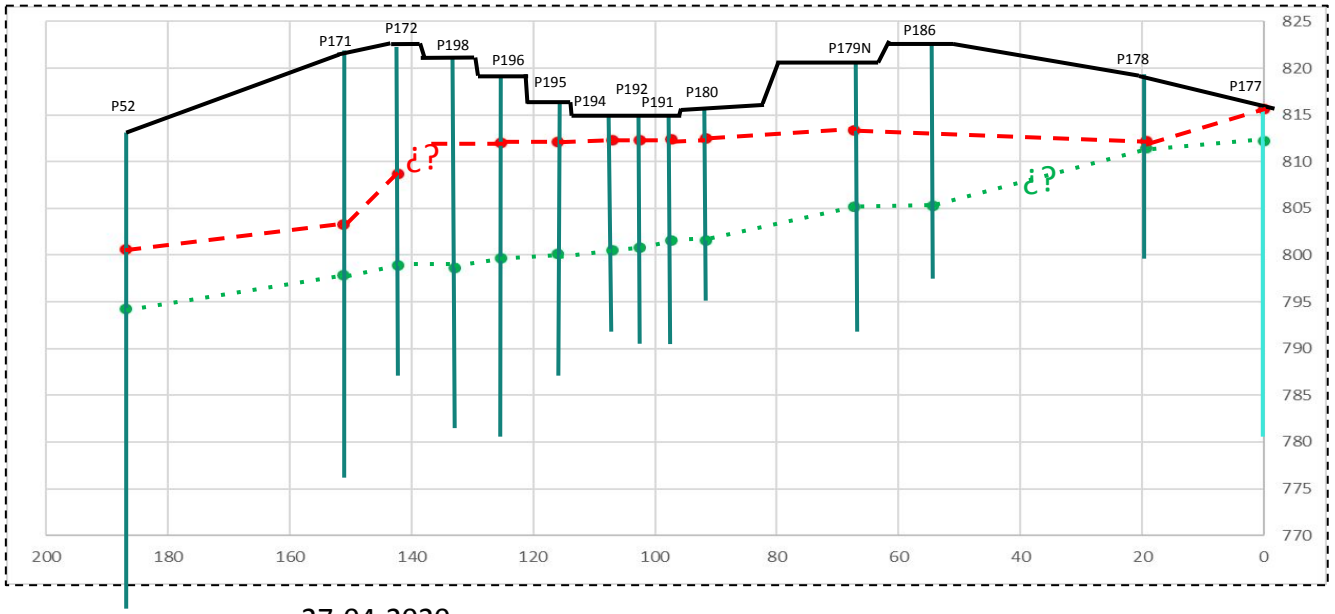


DRILLING AND TESTING BOREHOLES

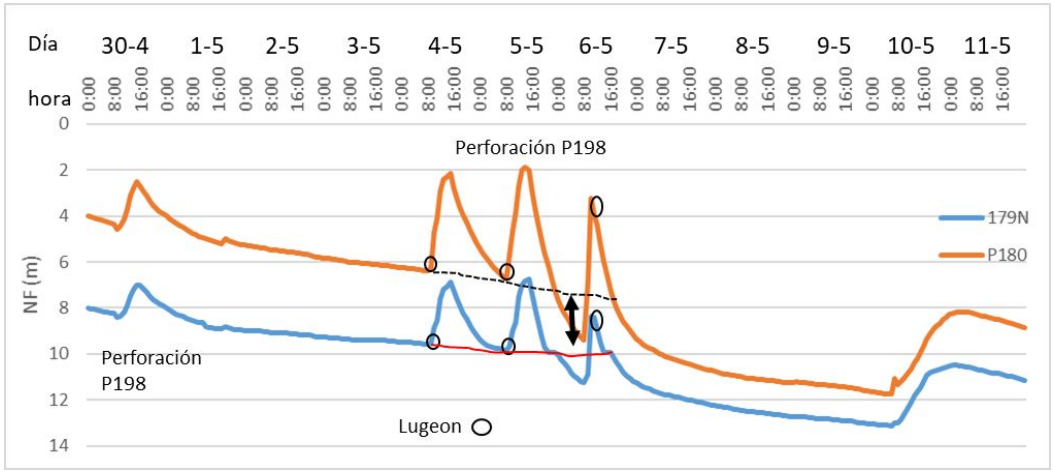
The hard reality

Topography determines where we can drill. The location of the wells also depends on accessibility. The distance between boreholes and their position in the layer depends on the availability of space

DRILLING AND TESTING BOREHOLES



Water table after the execution of P198 borehole

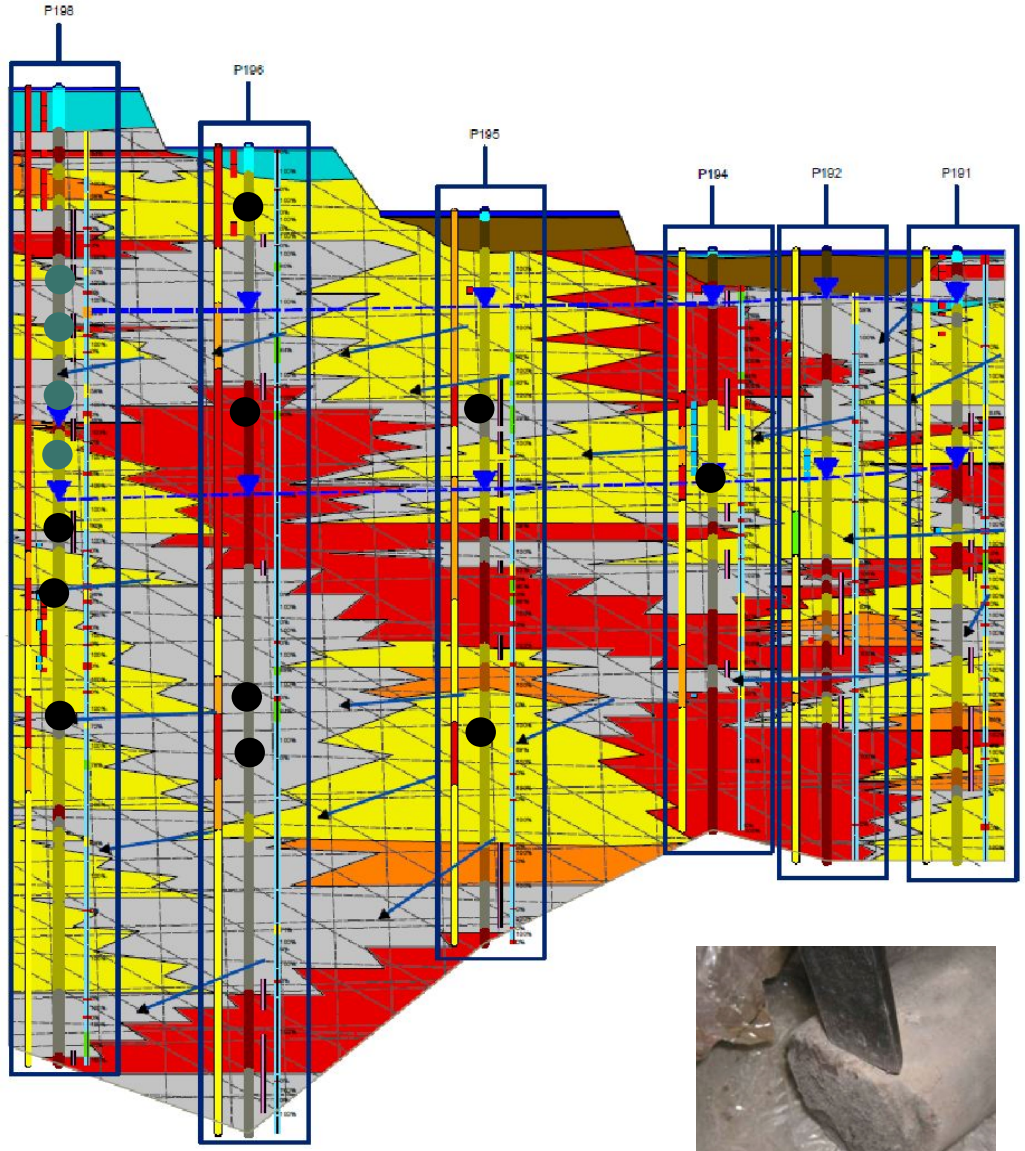


Water table behavior during the drilling of borehole P198 in the wells upstream of the test cell. Continuous measurements with divers. Lugeon test 2 between 24.3 and 29.3 meters in P198.

DRILLING AND TESTING BOREHOLES

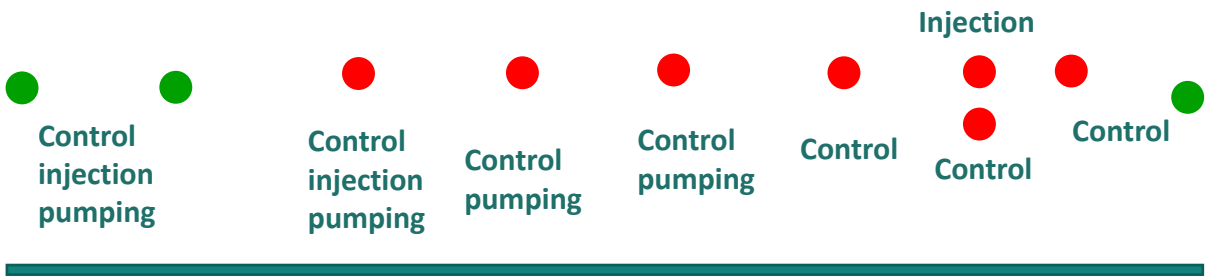
Lithostratigraphic profile and DNAPL distribution

GEOLOGICAL UNITS:
- Concrete platform
- Breakwater
- Fill and disturbance soils
- Sandy siltstones
- Sandstones
- Conglomerates of siltstone matrix
- Sandstone matrix conglomerates



- 78 Merc extractions are performed in 7 boreholes taking rock samples in fracture faces.
- The boreholes initially selected as injection points do not show significant concentrations, Apparently, there is no DNAPL in the axis of the ravine.
- The cell is enlarged, and a further borehole is drilled downstream (P198).
- Maximum observed COCs concentrations are 49 gr/m^2 of fracture.
- In P195-P196-P198 there are reliable evidences of residual DNAPL.

TEST CELL - DISTRIBUTION OF BOREHOLES

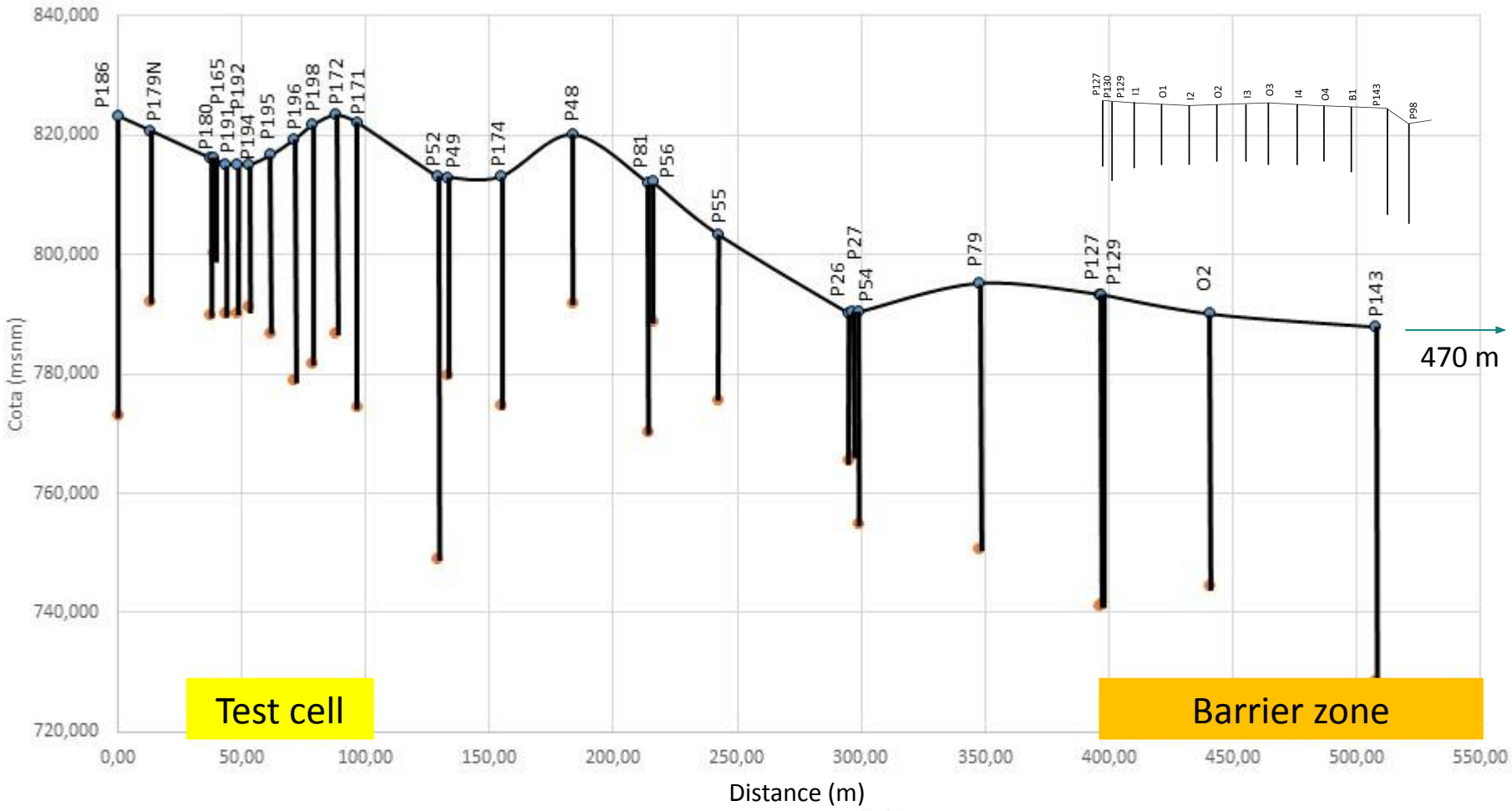


TEST CELL - DISTRIBUTION OF BOREHOLES

East

SCHEMATIC LONGITUDINAL PROFILE - SOUNDINGS IN LAYER M

West



470 m

Gállego river

HYDROGEOLOGICAL TESTS

Test objectives: connectivity between boreholes, speed of response to level changes, conditioning factors (lithological, structural, barriers, etc.) for flow and connectivity, admissible injection and pumping flow rates, approximate necessary volumes, and injection and pumping strategies.

Constraints - basic site characteristics:

- ✔ **Heterogeneous fractured medium.**
- ✔ **Aquifer delimited by low permeability levels. Width around 1 meter and depth 25-50 meters.**
- ✔ **The sedimentological arrangement (fluvial-deltaic medium with conglomerates, sandstones and siltstones) generates zones of variable permeability in the three directions of the aquifer.**
- ✔ **On the western edge of the cell there is a partial cement-bentonite screen that randomly modifies the connectivity between boreholes.**
- ✔ **There are fractures with residual and mobile DNAPL in the vadose zone in low water.**
- ✔ **Small storage capacity, rapid rise of the water table and north-south communication with other layers.**

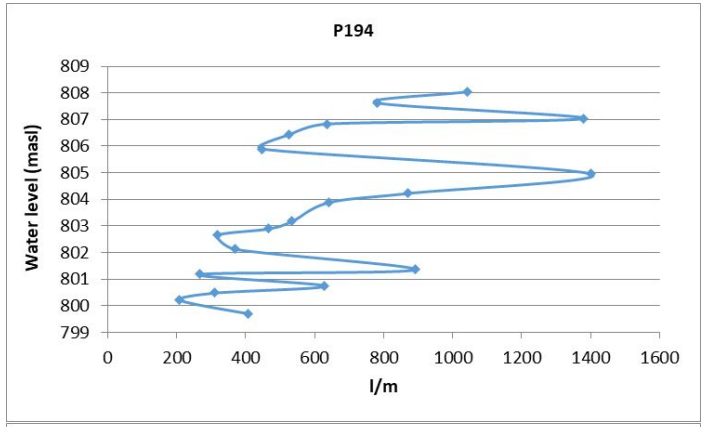
No criteria (boundary conditions) are met that allow the application of classical hydrogeological methodologies of testing and calculation for porous or fractured media.

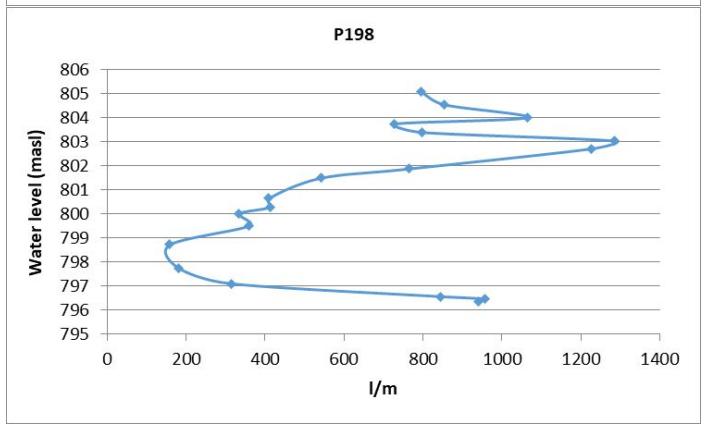
7 Hidrogeological Tests:

- ✔ **Injection at P192**
- ✔ **Pumping test at P171**
- ✔ **Injection test at P192 and P195**
- ✔ **Injection test in P192-P195 (packer P198**
- ✔ **Injection test in P198 (packer in P198, P195 and P192)**
- ✔ **Injection test at P198 and pumping at P192 and P195 (packer at P195 and P198)**
- ✔ **Pumping test at P171-P198**

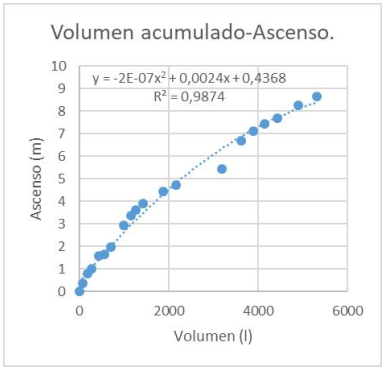
HYDROGEOLOGICAL TESTS

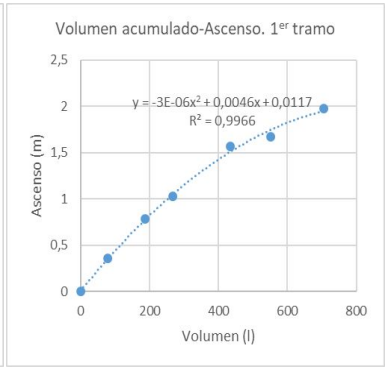
Admitted volume per meter height

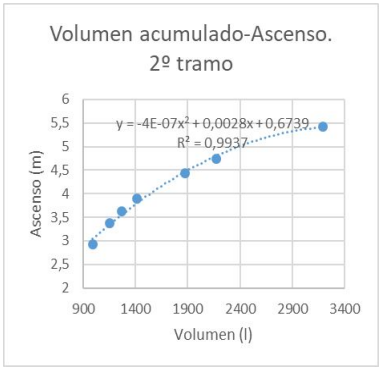


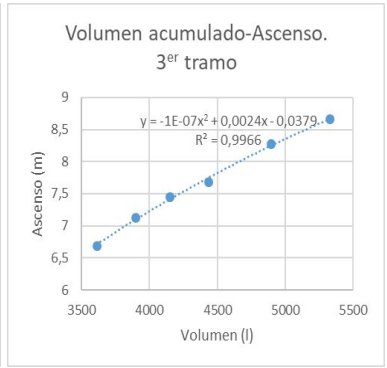


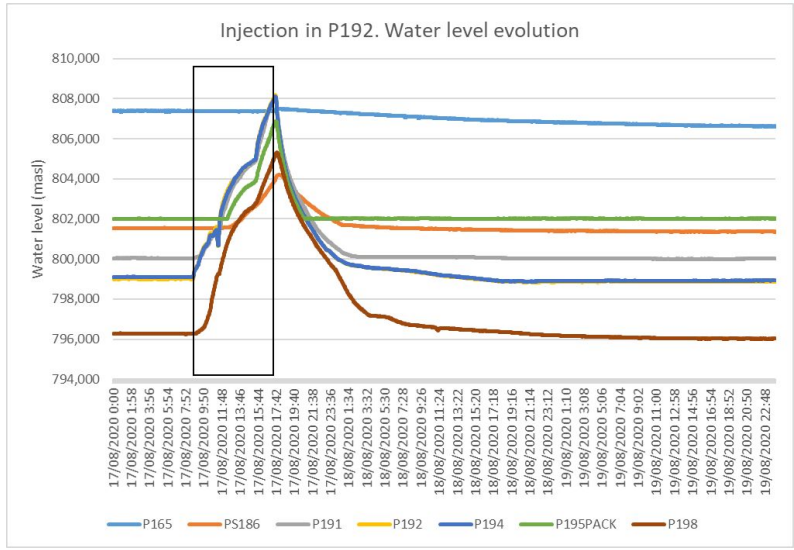
Water level elevation trends in borehole P192 as a function of cumulative volume.









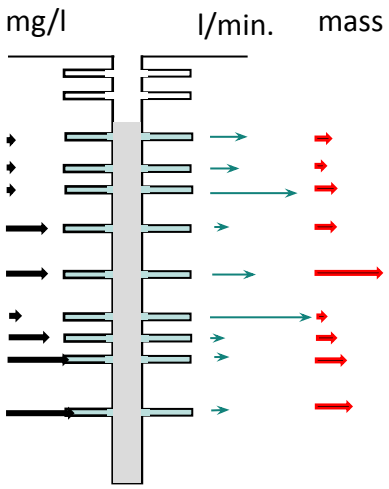


Borehole	Distance to P192 (m)	Upgrade level (m)	Delay (hours) Start	Max	Descent	Velocity (m/day)
P79	299,02	2,19	6,2	23,3	93	1376
P127	347,81	4,34	6,2	40,3	102	1533
P129	348,4	3,83	8,2	40,3	107	1166
O2	392,63	3,39	7,2	43,3	107	1292

HYDROGEOLOGICAL TESTS CONCLUSIONS

- In injection, the phreatic fill is vertical, above the initial level. The rise in levels is controlled by the density and opening of the fractures in each section and the lithostratigraphy. Low-water injection ensures that the injected fluids are distributed throughout the vadose zone up to the selected maximum elevation.
- To reach the target elevations, it is necessary to inject a flow rate close to 1000 L/hour. The balance between inflow (injection) and outflow (downstream flow) is 16 L/min and can be lowered to between 6-10 L/min with packer at P198.
- Circulation occurs preferentially between elevations 796.5-798 m at P194 and in a band between 796 and 800 m downstream, towards higher elevations the ascent is vertical. Below elevation 795 m there is no circulation.
- In the cell, the average velocity, established according to the recovery of the initial conditions of conductivity and temperature, is between 5 and 10 m/hour.
- Downstream, the level responses are very fast, so it can be expected that this is a pressure adjustment. Velocities of 251,260 and 171 meters/day are estimated. Tracer tests are needed to establish the real arrival time of the injected fluids.
- The pumping at P171-P172 to reach a steady state should be less than 50 l/hour, increasing in the upstream input to maintain equilibrium in the extraction.

TRACER TESTS



OBJECTIVES:

- ✔ Injection conditions to reach the target level and a residence time of several hours.
- ✔ Preferential routes, how the tracer moves downstream, depths at which it moves, mass and transit time.
- ✔ Injection and pumping flow rates
- ✔ Areas with presence of DNAPL
- ✔ Recovery rate
- ✔ Injection, pumping, and isolation strategies (packer)

Reagents:

- **Salt (ClNa): 5-10 g/l. conductivity 14 mS/cm.**
- **Bromide: 0.4 g/l.**
- **1-Heptanol: 500 ppm**

TRACER TESTS

- **INJECTION TEST IN P192:** Injection into a complete borehole. Check that the injectable flow is distributed mainly to saturate the vadose zone and the upper part currently occupied by the phreatic. Detect the arrival to boreholes downstream of the test cell to assess the response time to apply control measures in the barrier zone before the arrival of surfactant.
- **INJECTION TEST AT P198:** Packer at P198, injection at P198 over packer, pumping at P171-P195 and P196. Check that the injectable flow rate to reach the maximum possible level at P198 and P196 without exceeding level 810 at P192. Balance downstream fluid losses with injection to maintain the maximum level as long as possible.
- **INJECTION TEST AT P198 BIS:** Injection at P198 over packer, double packer at P198, pumping at P171 and P172 and recirculation to P198, Pumping for recovery at P171, P172, P192, P195 and P196. Balance downstream fluid losses with injection to maintain maximum level as long as possible. Optimize tracer recovery.
- **INJECTION-PUMPING TEST IN P172 AND P171:** phase 1 packer in P198 and P171, injection in P172, pumping P171 and P172. Phase 2: injection and pumping in P171 under packer.Establish the feasibility of injection and pumping in short times in the same borehole and the recovery yields. Check that the injectable flow rate to maintain the level at around 15 meters depth (beginning of the possible presence of DNAPL) in P171 and P172 . Balance downstream fluid losses with injection to maintain the maximum level as long as possible.
- **BOTTOM OF CELL INJECTION-PUMMING TEST:** Injection in P196 under packer and pumping in P195 and P198 under packer. Pumping in the three boreholes after injection.Establish if there is connection in the deepest section of wells P195 to P198. Check the injectable and pumpable flow rate to maintain stable levels in the three boreholes above the packers.

TRACER TESTS – TEST MONITORING

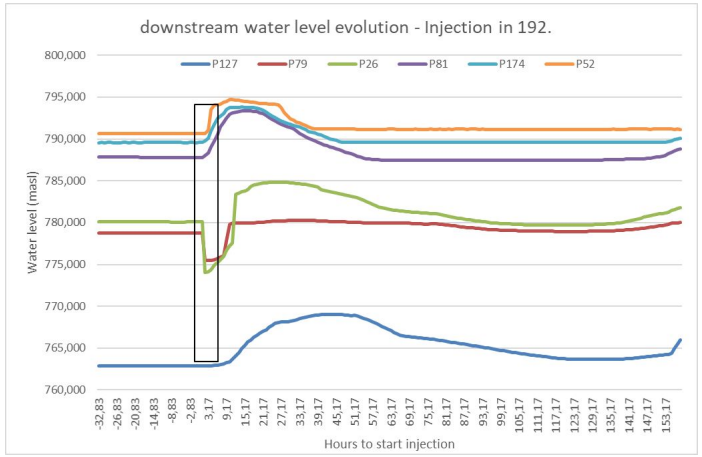
Control parameters:

- **Conductivity: vertical profiles, indicates arrival time and dispersion rates.**
- **Bromide: recovery rate, mass balance between injection and pumping.**
- **1-Heptanol: preferential retention in DNAPL. indicator of DNAPL presence.**

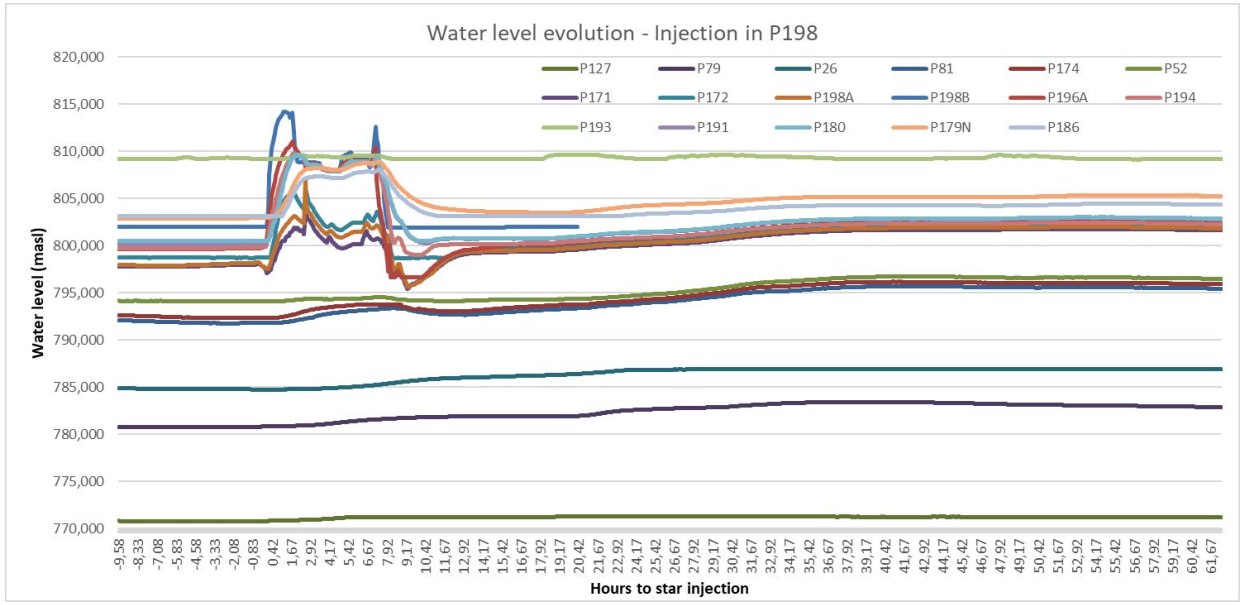
Methodology

- **Authomathic level, temperature, and conductivity measurements probes (divers)**
- **Measurement with a manual level probe**
- **Manual vertical profiling with conductivity probe**
- **Sampling at target levels, with bladder pump and discrete interval sampler**
- **Control of injected and pumped volumes/time**
- **Immediate in-lab determination of physicochemical parameters and tracer concentration**

TRACER TESTS – WATER LEVEL TREND



Examples of level monitoring

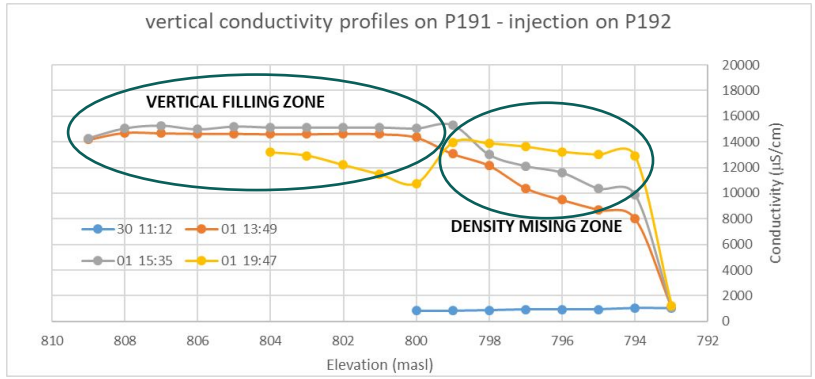


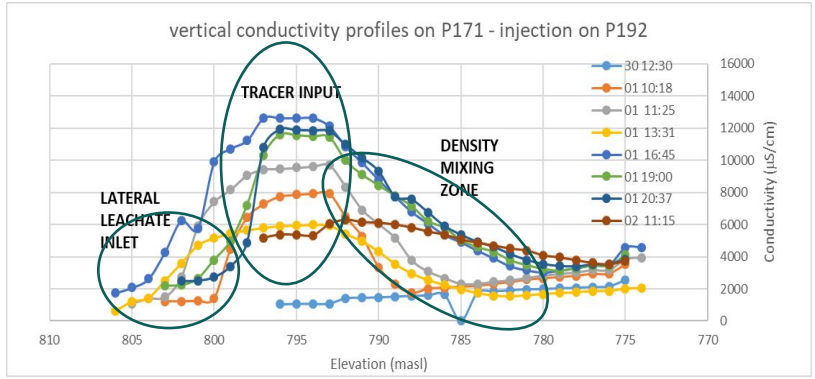
Boreholes response, arrival velocities.

BOREHOLE	Distance to P192 (m)	delay 1st elevation (min)	Speed (m/h)	peak level delay (min)	Speed (m/h)
P186	-48,16	80	36,12	510	5,67
P179N	-35,31	35	60,53	495	4,28
P180	-10,85	20	32,56	65	10,02
P191	-5,16	15	20,63	60	5,16
P192	0,00				
P194	4,48				
P195	13,50				
P196	22,82				
P198	30,35				
P172	39,62	40	59,43	40	59,43
P171	48,59				
P52	80,83	120	40,42	680	7,13
P174	106,16	110	57,91	570	11,17
P81	165,72	90	110,48	815	12,20
P26	316,01	120	158,01	1330	14,26
P79	357,40	120	178,70	1750	12,25
P127	398,05	290	82,35	2450	9,75

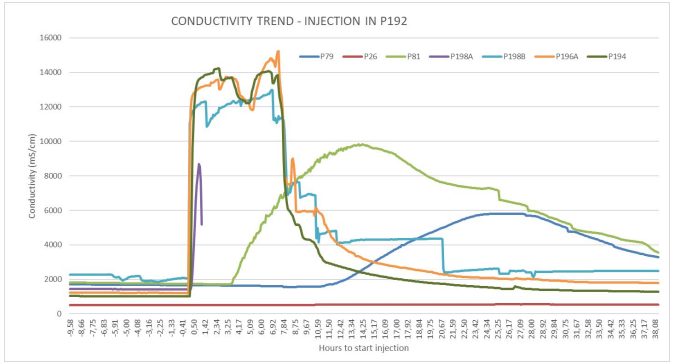
TRACER TESTS – CONDUCTIVITY TREND

Conductivity monitoring - vertical profiles

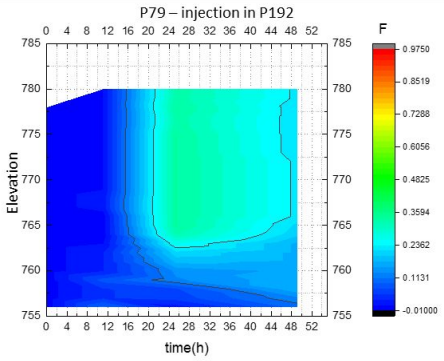


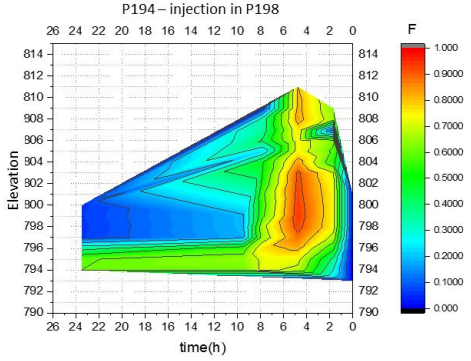


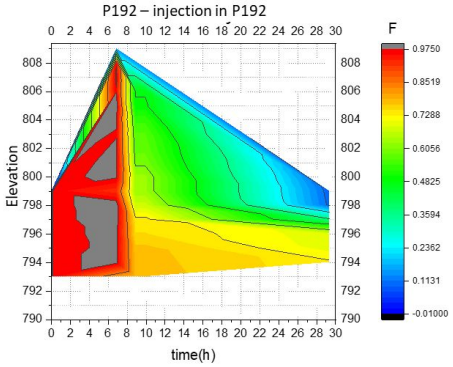
Conductivity monitoring - continuous sensor



Conductivity monitoring - 2D: time-elevation

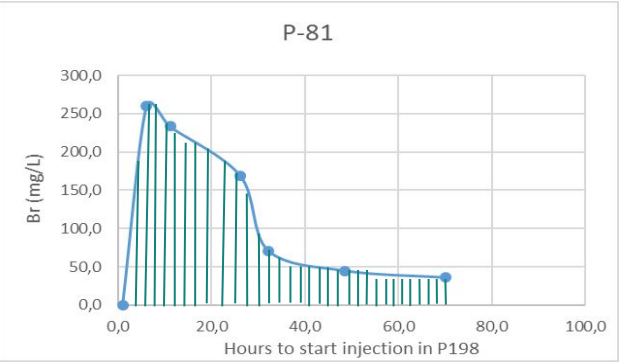


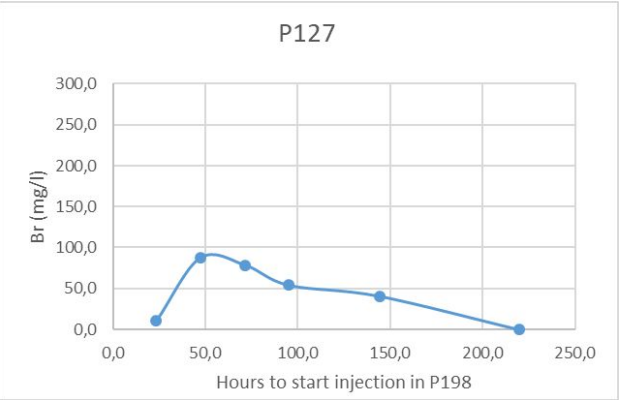


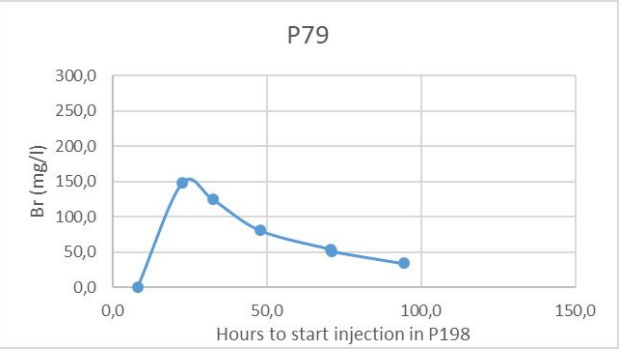


$$F_t = \frac{(k_t - k_o)_{elevation}}{k_{injection}}$$

TRACER TESTS – MASS BALANCE







Total mass transmitted downstream of P171 for a conservative compound (in our case bromide). We assume 3000 liters with 450 mg/l, i.e. 1,350,000 mg).

p81						
horas inicio inyeccion	Br IC (mg/L)	t_x-$t_{(x-1)}$ (h)	$(Br_x+Br_{(x+1)})/2$	$\int_x^{x+1} C_{Br}\,dt$	X =V $^{tx}_{tx-1}$	Q (l/h)
1	0	0	0	0	0	0
6,1	260,5	5,1	130,3	669,2	268,7	52,3
11,2	233,4	5	247	1243	499,2	99,2
26,2	168,8	15,1	201,1	3029,6	1216,7	80,8
32,2	71,1	6	120	713,7	286,6	48,2
48,7	44,6	16,5	57,9	953,6	382,9	23,2
70,1	35,8	21,4	40,2	861,2	345,9	16,1
				7470,2	3000	
Horas pluma	Q med (l/h)	$Q_{med} * \int_x^{x+1} C_{Br}\,dt$ (gr)	% Masa Br_0			
69,1	43,4	324.305	24			

	dist (m)	Br (mg/l)
P55	164	296
P79	269	150
P127	317	90
I1	328	93
O1	341	75
O2	362	55,4
P98	458	33
P146	507	32
P140	867	0

TRACER TESTS – CONCLUSIONS

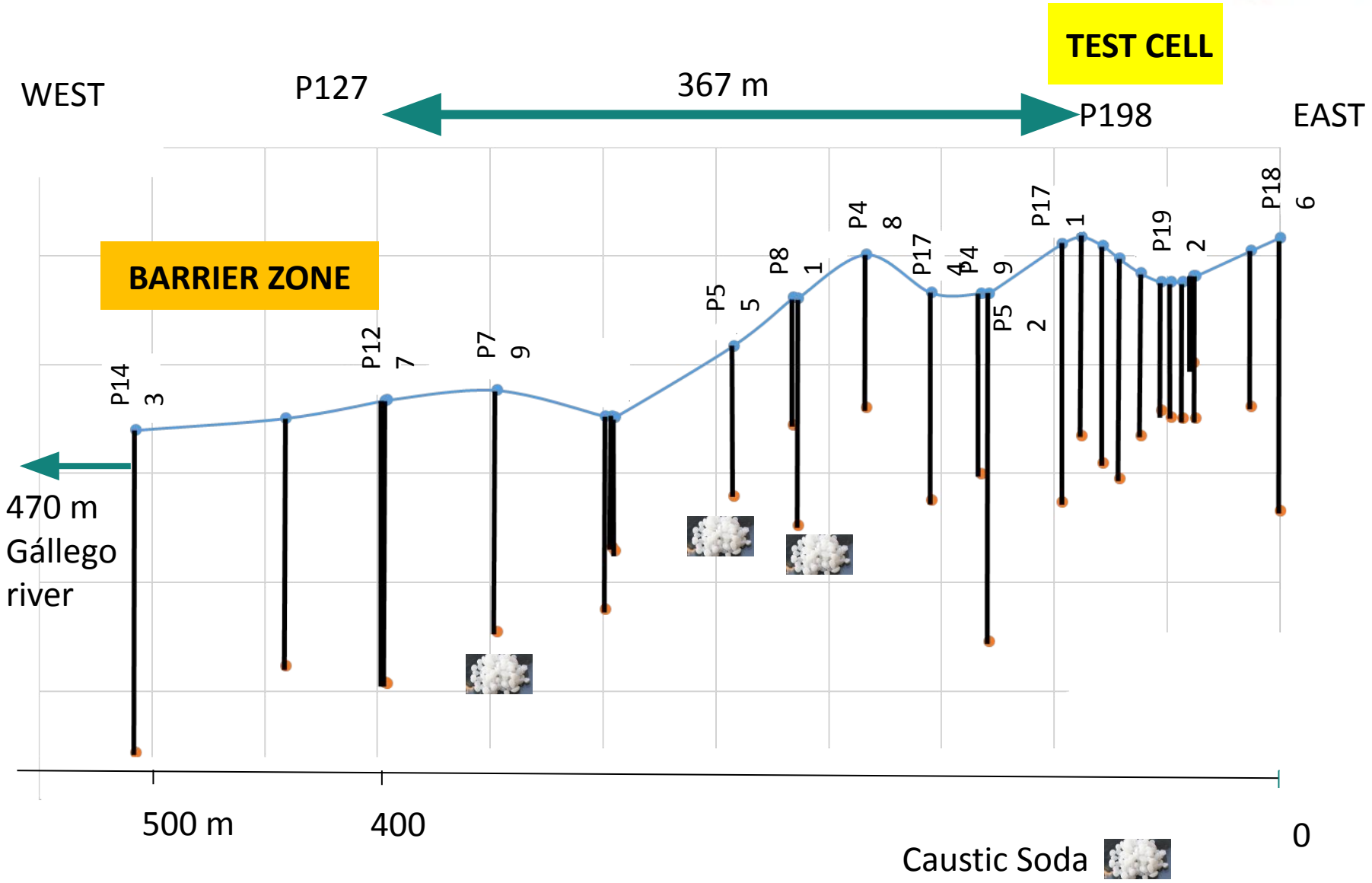
- **Injected flow rates are distributed mainly vertically, saturating the vadose zone.**
- **It is necessary to inject at P198** to reach some fractures with the possible presence of DNAPL between P195 and P198.
- The **useful permeability** in the cell zone above the water table at low water up to about 809 is **0.4%.** The **volume stored upstream of borehole P198** is approximately **2.4 m3,** with a **flow rate** of approximately **14 l/min downstream** to maintain equilibrium levels.
- The use of **packer in P198** allows to decrease the downstream **flow rates** by at least **5 l/min.**
- The **tracer recovery rate** is less than **30%** if no measures are taken. With the use of **packer at P198 and pumping** (electric pump) **and recirculation at P171 and P172 it can approach 80%.**
- In the cell zone the flow is practically piston-like with increased downstream dispersion.
- The **flow velocity downstream** of the test cell, considering the first response in the level modification, varies between **40 and 180 m/h**, it does not respond to the real arrival of fluids but to an adjustment of pressures. Depending on the actual **arrival of tracer**, the average **velocity** varies between **15 m/h for the first tracer flows** and **7 m/h for the concentration peak**.
- From the beginning of the injection, the **response time to adopt measures in the barrier zone** is approximately **27 hours**, **reaching the peak at 52 hours and prolonging the affected flow up to 5 days** from the beginning of the injection, always considering that no control measures are adopted upstream of the barrier zone.

BARRIER ZONE - OPERATION

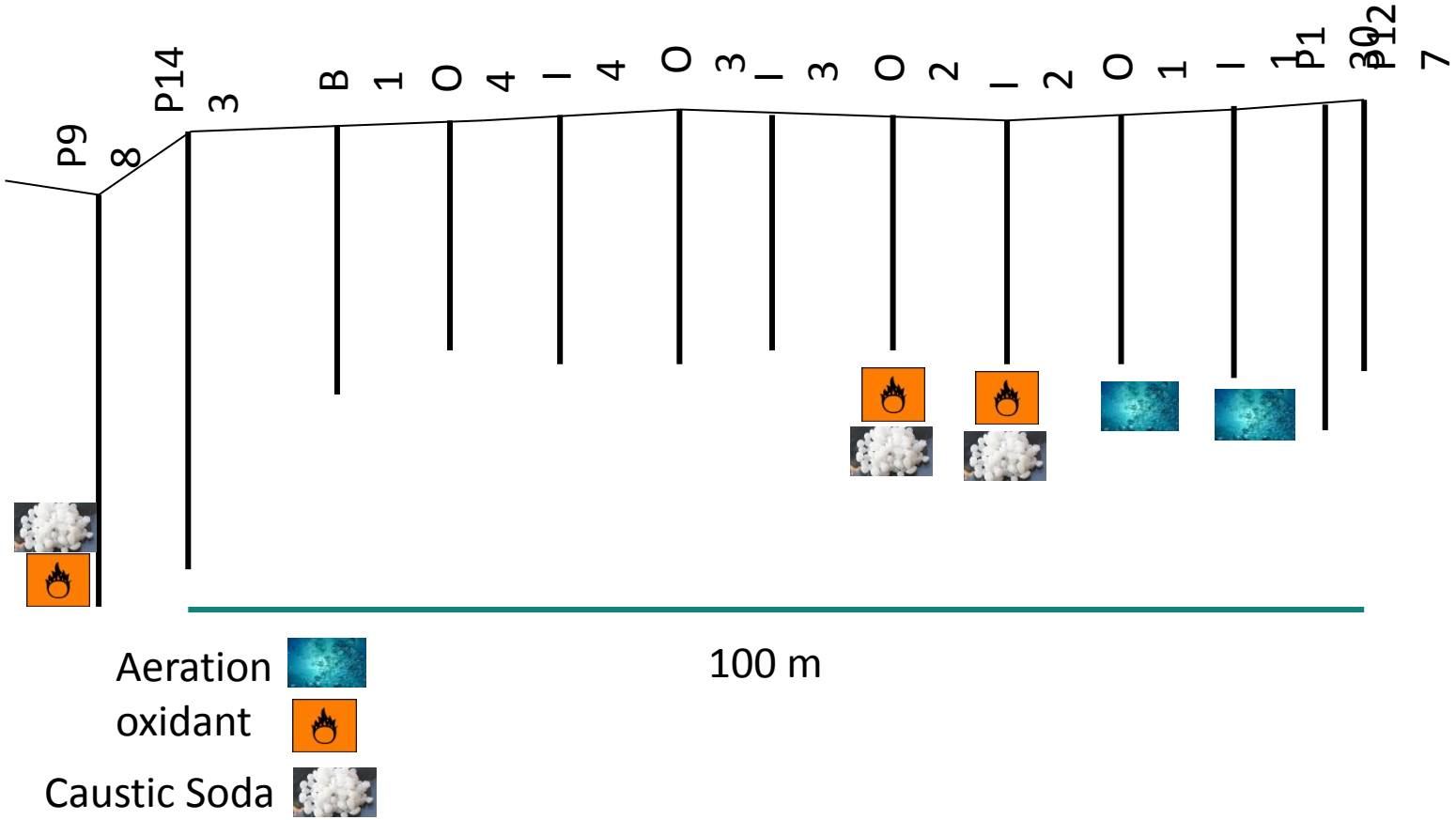
OBJECTIVES: Once the mass of surfactant that can reach the barrier zone (conservative behavior assumed) and the arrival time are established, tracer is injected into the test cell and the expected surfactant ratio at the beginning of the barrier zone. The effectiveness of the barrier treatments is tested

DOWNSTREAM TREATMENT
soda in P81, P55 and P79
surfactant at P127
Aeration and gas collection in I1 and O1
Persulfate and soda in I2 and O2

BARRIER ZONE - OPERATION



BARRIER ZONE - OPERATION



BARRIER ZONE - CONCLUSIONS

- **NaOH injection** between the cell and the barrier zone maintains strongly alkaline conditions, with a very **efficient transformation of HCHs to trichlorobenzenes**.
- The concentrations of **dichlorobenzenes grow** higher than those of trichlorobenzenes, which seems to indicate that the **alkaline hydrochlorination** has gone to higher dechlorination rates than those cited in the literature.
- **Aeration** gives good performance in the **removal of benzene and chlorobenzene**.
- **Alkalinization** also **degrades the surfactant partially**, which favors the removal of contaminants in the barrier zone.
- **Applying aeration and oxidation with persulfate in the same wells** favors oxidation kinetics (thermal activation of persulfate), improves evaporation performance (lighter compounds) and favors diffusion of the oxidant.
- The **surfactant is non-conservative** and will be largely retained by irreversible adsorption during its travel downstream of the test cell and is removed in the barrier zone, **minimizing risks to the receiving stream**.
- The great heterogeneity of this type of aquifer makes it essential to achieve an exhaustive knowledge of the environment, with **hydrogeological and tracer tests to adjust injection and pumping strategies**, and particularly the adoption of downstream measures to ensure that the mobilized surfactant and contaminants do not reach the receiving environment.

14th International HCH and Pesticides Forum

THANK YOU FOR YOUR ATTENTION

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